

PATENT SPECIFICATION

(11) 1317732

DRAWINGS ATTACHED

- (21) Application No. 18162/70 (22) Filed 16 April 1970
 (31) Convention Application No. 822847 (32) Filed 16 April 1969 in
 (33) United States of America (US)
 (44) Complete Specification published 23 May 1973
 (51) International Classification H05B 33/12
 (52) Index at acceptance

C4S 311 33Y 43Y 68X 68Y 703 708 709 70Y 711 714
 715 717 719 721 731 733 735 737 739 753 755
 757 75Y 764 767 769 760 76Y 770 771 782 783



PATENTS ACT 1949

SPECIFICATION NO 1317732

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act 1949, to Specification No 1263185

THE PATENT OFFICE
 1 February 1974

R 72294/5

10 State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

15 The invention relates to electroluminescent devices. Contemplated use is in display devices on communication and computer equipment.

20 There has been produced an electroluminescent apparatus which enables the radiation produced to be varied, this being described and claimed in British Patent Specification 18161/70 (Serial No. 1317731). This patent claims an electroluminescent apparatus for producing radiation in the visible spectrum including an electroluminescent device comprising a semiconductor p-n junction diode 25 capable of producing infrared radiation within the absorption spectrum for Yb^{3+} when biased, said diode being provided with a phosphor on a surface thereof for converting the infrared radiation to radiation in the visible spectrum said phosphor containing the cation pair Yb^{3+} — Er^{3+} , wherein the said phosphor has either at least two anion sites per unit cell which are differently populated in at least 30 one percent of the unit cells of the said phosphor, or at least one anion vacancy per unit cell in at least 1% of the unit cells of the phosphor and wherein the phosphor consists of a fluorohalide, the halide in the fluorohalide being other than fluoride, or an oxyhalide or a mixture thereof, the phosphor 35 containing either a cation percent of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and

50 — in which the said phosphor is capable of converting said infrared radiation to visible emission by at least a two excitation process each producing a different emission wavelength and each of which process involves a multiphoton process which is at least a two stage excitation, and in which the electroluminescent device is in combination with a circuit varying the power level of said infrared radiation so as to alter the relative 55 amounts of visible radiation produced by the said two processes.

60 There is a recognized need for a low power level, long lifetime electroluminescent device. While several avenues have been investigated, many consider the direct emitting PN junction semiconductor diode to be the most promising.

65 There is a large body of reported work considering gallium phosphide diodes. Depending on the dopant used, GaP junctions may emit in the red or the green. The red emitting device is more efficient and its development has now attained a fair level 70 of sophistication. Recently, such a diode operating at an efficiency of 3.4% was reported; I. Ladany, Electro-Chemical Society Meeting, Montreal, October 11th, 1968, Paper 610, RNP. 75

80 Silicon-doped GaAs diodes are several times as efficient (up to about 20% at room temperature) but emit at infrared rather than visible wavelengths. The possibility exists that the GaAs infrared output may be up-converted to a visible wavelength with reasonable conversion efficiency.

It was recently announced that appreciable

SEE ATTACHED SLIP

PATENT SPECIFICATION

(11) 1317732

DRAWINGS ATTACHED

- (21) Application No. 18162/70 (22) Filed 16 April 1970
 (31) Convention Application No. 822847 (32) Filed 16 April 1969 in
 (33) United States of America (US)
 (44) Complete Specification published 23 May 1973
 (51) International Classification H05B 33/12
 (52) Index at acceptance



C4S 311 33Y 43Y 68X 68Y 703 708 709 70Y 711 714
 715 717 719 721 731 733 735 737 739 753 755
 757 75Y 764 767 768 769 76Y 770 771 782 783
 78Y

- (72) Inventors WILLIAM HENRY GRODKIEWICZ
 SHOBHA SINGH and
 LEGRAND GERARD VAN UITERT

(54) ELECTROLUMINESCENT DEVICES

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organised and existing under the laws of the State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to electroluminescent devices. Contemplated use is in display devices on communication and computer equipment.

There has been produced an electroluminescent apparatus which enables the radiation produced to be varied, this being described and claimed in British Patent Specification 18161/70 (Serial No. 1317731). This patent claims an electroluminescent apparatus for producing radiation in the visible spectrum including an electroluminescent device comprising a semiconductor p-n junction diode capable of producing infrared radiation within the absorption spectrum for Yb^{3+} when biased, said diode being provided with a phosphor on a surface thereof for converting the infrared radiation to radiation in the visible spectrum said phosphor containing the cation pair Yb^{3+} — Er^{3+} , wherein the said phosphor has either at least two anion sites per unit cell which are differently populated in at least one percent of the unit cells of the said phosphor, or at least one anion vacancy per unit cell in at least 1% of the unit cells of the phosphor and wherein the phosphor consists of a fluorohalide, the halide in the fluorohalide being other than fluoride, or an oxyhalide or a mixture thereof, the phosphor containing either a cation percent of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and

from 5 cation % Yb^{3+} to 50 cation % Yb^{3+} , or from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and 1/50 cation % Ho^{3+} to 5 cation % Ho^{3+} together with at least 5 cation % Yb^{3+} and in which the said phosphor is capable of converting said infrared radiation to visible emission by at least a two excitation process each producing a different emission wavelength and each of which process involves a multiphoton process which is at least a two stage excitation, and in which the electroluminescent device is in combination with a circuit varying the power level of said infrared radiation so as to alter the relative amounts of visible radiation produced by the said two processes.

There is a recognized need for a low power level, long lifetime electroluminescent device. While several avenues have been investigated, many consider the direct emitting PN junction semiconductor diode to be the most promising.

There is a large body of reported work considering gallium phosphide diodes. Depending on the dopant used, GaP junctions may emit in the red or the green. The red emitting device is more efficient and its development has now attained a fair level of sophistication. Recently, such a diode operating at an efficiency of 3.4% was reported; I. Ladany, Electro-Chemical Society Meeting, Montreal, October 11th, 1968, Paper 610, RNP.

Silicon-doped GaAs diodes are several times as efficient (up to about 20% at room temperature) but emit at infrared rather than visible wavelengths. The possibility exists that the GaAs infrared output may be up-converted to a visible wavelength with reasonable conversion efficiency.

It was recently announced that appreciable

SEE ATTACHED SLIP

output at a visible wavelength had been obtained by use of a conversion phosphor coating on such a silicon doped GaAs diode, see S. V. Galginitis et al, International Conference of GaAs, Dallas, October 17th, 1968, "Spontaneous Emission Paper No. 2". The coating, which depends on a two-photon process, utilizes the ytterbium-erbium ion pair in a host of lanthanum fluoride.

In the coated device, infrared emission with a peak wavelength at about 0.93 μ (micron) is absorbed by Yb³⁺ with a peak absorption at 0.98 μ . Transfer and two-photon excitation results in Er³⁺ green emission at 0.54 μ .

While the coated GaAs diode represents a clear technological advance, efficiency at this stage in its development is not equal to that of the best GaP diodes with the latter operating in the red.

In accordance with the invention there is provided an electroluminescent device for producing radiation in the visible spectrum including a semiconductor p-n junction diode capable of producing infrared radiation when biased, said diode being provided with a phosphor on a surface thereof for converting said infrared radiation to radiation in the visible spectrum, the said phosphor consisting of an oxyhalide and/or a fluorohalide host material, the halide in the fluorohalide being other than fluoride, and containing at least 5 cation percent of Yb³⁺ based on the total cation content of the phosphor, in which either the phosphor contains at least two anion sites per unit cell which are differently populated in at least one percent of the unit cells of said phosphor, or there is at least one anion vacancy per unit cell in at least one percent of the unit cells of the said phosphor, and wherein the phosphor further contains at least one of the following cations in the specified concentration ranges, selected from the group which consists of from 1/16 cation % Er³⁺ to 20 cation % Er³⁺, from 1/50 cation % Ho³⁺ to 5 cation % Ho³⁺ and 1/16 cation % Tm³⁺ to 5 cation % Tm³⁺.

Throughout the specification it is intended that the Yb, Er, Ho and Tm concentration ranges as above, apply independently to each of the fluorohalide and oxyhalide components when in a mixture.

In embodiments of the invention, GaAs infrared diodes provided with a conversion coating of a phosphor compound to be described herein show increased visible output as compared with LaF₃ coated devices. Improved conversion efficiency is attributed, at least in part, to the anisotropic nature of the host environment due to a non-symmetrical array of anions or differences in neighbouring anions with its attendant crystal field splitting for the Yb³⁺ absorption spectra.

In oxychloride and fluorochloride host materials, relatively broad Yb³⁺ absorption

peaks at about 0.94 μ permit a particularly good match for existing silicon-doped GaAs diode emissions.

Depending on the structure and the concentration of sensitizer (Yb³⁺) and activator (Er³⁺) ions in such hosts, blue, green or red fluorescence can be realized. Strong excitation may result in appreciable green and blue emission at wavelengths of about 0.55 and 0.41 μ , respectively, and strong emission in the red at a wavelength of about 0.66 μ . However, for example, in the YOCl and Y₃OCl₇ hosts, fluorescence appears red or green, respectively, to the eye for the lowest levels of discernible emission. Improvement in attainable brightness in the green in such cases and/or an adjustment in the apparent output colour may result from the addition of limited quantities of holmium (Ho³⁺) which typically emits at about 0.54 μ in the green.

Attention to the considerations set forth above dictates desirable ranges of activator (Er³⁺, Ho³⁺ and/or Tm³⁺) and sensitizer (Yb³⁺) ion contents. Together, these may be less than the total cation content as various inactive cations such as yttrium, lanthanum, lutecium or gadolinium may be utilized.

For a better understanding of the invention, reference is made to the accompanying drawing in which:

FIG. 1 is a front elevational view of an infrared emitting diode having a phosphor converting coating in accordance with one embodiment of the invention; and

FIG. 2 is an energy level diagram in ordinate units of wave numbers for the ions Yb³⁺, Er³⁺, Ho³⁺ and Tm³⁺ within the crystallographic environment provided by a composition herein.

Gallium arsenide diode 1 containing PN junction 2, defined by P and N regions 3 and 4, respectively, is forward-biased by planar anode 5 and ring cathode 6 connected to power supply not shown. Infrared radiation is produced by junction 2 under forward-biased conditions, and some of this radiation, represented by arrows 7, passes into and through layer 8 of a phosphorescent material. Under these conditions, some part of radiation 7 is absorbed within layer 8, and a major portion of that absorbed participates in a two-photon or higher order photon process to produce radiation at visible wavelengths. The portion of this reradiation which escapes is represented by arrows 9.

The main advantage of the defined phosphors is best described in terms of the energy level diagram of FIG. 2. While this energy level diagram is a valuable aid in the description of the embodiments, two reservations must be made. The specific level values, while reasonably illustrative of those for the various included compositions of the noted type, are most closely representative of the oxychloride systems either of the YOCl or

Y₃OCl₇ stoichiometries. Also, while the detailed energy level description was determined on the basis of carefully conducted absorption and emission studies, some of the information contained in the figure is not certain. In particular, the excitation routes for the 3 and 4 photon processes are not certain although it is clear that some of the observed emission represents a multiple photon process in excess of doubling. The diagram is sufficient for its purpose; that is, it does describe the common advantages of the included host materials and, more generally, of the included phosphors in the terminology which is in use by quantum physicists.

For example, phosphor coating 8 may contain an additional inert ingredient or ingredients serving, for example, to improve adhesion to the substrate 4 and/or to reduce light

scattering between particles where coating 8 is particulate. Still another purpose which may be served by an inert ingredient is to "encapsulate" the coating material so as to protect it from any harmful environment.

FIG. 2 contains information on Yb³⁺, Er³⁺, Ho³⁺ and Tm³⁺. While the pairs Yb³⁺—Ho³⁺ and Yb³⁺—Tm³⁺ are not the most efficient for energy up conversion, the former does provide a strong green fluorescence and enables a desirable colour shift and improvement in efficiency when included as an ancillary pair with Yb³⁺—Er³⁺. Further, the Yb³⁺—Tm³⁺ couple provides a source of blue fluorescence.

The ordinate units are in wavelengths per centimetre (cm⁻¹). These units may be converted to wavelength in angstrom units (Å) or microns (μ) in accordance with the relationship:

$$\text{Wavelength} = \frac{10^8}{\text{Wave numbers}} \text{ Å} = \frac{10^4}{\text{Wave numbers}} \mu.$$

The left-hand portion of the diagram is concerned with the relevant manifolds of Yb³⁺ in a host of the invention. Absorption in Yb³⁺ results in an energy increase from the ground manifold Yb³⁺F_{7/2} to the Yb³⁺F_{5/2} manifold. This absorption defines a band which includes levels at 10,200 cm⁻¹, 10,500 cm⁻¹ and 10,700 cm⁻¹. The positions of these levels are affected by the crystal field splitting within the structures having at least one each of two different anions or at least one anion vacancy per unit cell or formula unit. In the oxychlorides, for example, they include a broad absorption which peaks at about 0.94 μ (10,600 cm⁻¹), there is an efficient transfer of energy from a silicon-doped GaAs diode (with its emission peak at about 0.93 μ).

The remainder of FIG. 2 is discussed in conjunction with the postulated excitation mechanism. All energy level values and all relaxations indicated on the figure have been experimentally verified.

Following absorption by Yb³⁺, of emission from the GaAs diode, a quantum is yielded to the emitting ion Er³⁺ (or as also discussed in conjunction with the figure, to Ho³⁺ or Tm³⁺). The first transition is denoted 11. Excitation of Er³⁺ to the ⁴I_{11/2} is almost exactly matched in energy (denoted by m) to the relaxation transition of Yb³⁺. However, a similar transfer, resulting in excitation of Ho³⁺ to Ho³⁺I₆ or Tm³⁺ to Tm³⁺H₆, requires a simultaneous release of one or more phonons (+P). The manifold Er³⁺I_{11/2} has a substantial lifetime, and transfer of a second quantum from Yb³⁺ promotes transition 12 to the Er³⁺F_{7/2} manifold. Transfer of a second quantum to Ho³⁺ or Tm³⁺ results in excitation to Ho³⁺S₂ or, after internal relaxa-

tion from Tm³⁺H₆ to Tm³⁺H₄ (by yielding energy as phonons in the matrix), excitation to Tm³⁺F₂ with simultaneous generation of phonon. Internal relaxation is represented on this figure by the wavy arrow (↘). In erbium, the second photon level (Er³⁺F_{7/2}) has a lifetime which is very short due to the presence of close, lower lying levels which results in rapid degradation to the Er³⁺S_{3/2} state through the generation of phonons.

The first significant emission of Er³⁺ is from the Er³⁺S_{3/2} state (18,200 cm⁻¹ or 0.55 μ in the green). This emission is denoted in the figure by the broad (double line) arrow A. The reverse of the second photon excitation, the nonradiative transfer of a quantum from Er³⁺F_{7/2} back to Yb³⁺ must compete with the rapid phonon relaxation to Er³⁺S_{3/2} and is not limiting. The phonon relaxation to Er³⁺F_{9/2} also competes with emission A and contributes to emission from that level. The extent to which this further relaxation is significant is composition dependent. The overall considerations as to the relationship between the predominant emissions and composition are herein discussed.

Green emission A at a wavelength of about 0.55 μ corresponds to that which has been previously observed for Er in LaF₃. In accordance with the embodiments, it has been shown that the structures having mixed anions or anion vacancies with large resulting anisotropic environments about the cations are characterised by large crystal field splittings which significantly improve the absorption of GaAs:Si emission by Yb³⁺. Large crystal field splittings also result in increased opportunity for internal relaxation mechanisms involving phonon generation which thus far have not

been found to be pronounced in comparable but more isotropic media. For Er^{3+} , this enhances emission B at red wavelengths. Erbium emission B is, in part, brought about by transfer of a third quantum from Yb^{3+} to Er^{3+} which excites the ion from $\text{Er}^4\text{S}_{3/2}$ to $\text{Er}^2\text{G}_{7/2}$ with simultaneous generation of a phonon (transition 13). This is followed by internal relaxation to $\text{Er}^4\text{G}_{11/2}$ which, in turn, permits relaxation to $\text{Er}^4\text{F}_{9/2}$ by transfer of a quantum back to Yb^{3+} with the simultaneous generation of a phonon (transition 13'). The $\text{Er}^4\text{F}_{9/2}$ level is thereby populated by at least two distinct mechanisms and indeed experimental confirmation arises from the finding that emission B is dependent on a power of the input intensity which is intermediate in character to that characteristic of a three-phonon process and that characteristic of a two-phonon process for the Y_2OCl_7 host. Emission B, in the red, is at about $15,250\text{ cm}^{-1}$ or $0.66\text{ }\mu$.

While emissions in the green and red are predominant, there are many other emission wavelengths of which the next strongest designated C is in the blue ($24,400\text{ cm}^{-1}$ or $0.41\text{ }\mu$). This third emission designated C originates from the $\text{Er}^2\text{H}_{9/2}$ level which is, in turn, populated by two mechanisms. In the first of these, energy is received by a phonon process from $\text{Er}^4\text{G}_{11/2}$. The other mechanism is a four-photon process in accordance with which a fourth quanta is transferred from Yb^{3+} to Er^{3+} exciting $\text{Er}^4\text{G}_{9/2}$ from $\text{Er}^4\text{G}_{11/2}$ (transition 14). This step is followed by internal relaxation to $\text{Er}^2\text{D}_{5/2}$ from which level energy can be transferred back to Yb relaxing Er to $\text{Er}^2\text{H}_{9/2}$ (transition 14').

Significant emission from holmium occurs only by a two-photon process. Emission is predominantly from Ho^2S_2 in the green ($18,350\text{ cm}^{-1}$ or $0.54\text{ }\mu$). A similar process in thulium also results in emission by a three-photon process (from Tm^4G_4 in the blue at about $21,000\text{ cm}^{-1}$ or $0.47\text{ }\mu$). The responsible mechanisms are clear from FIG. 2 and the foregoing discussion.

Since the phosphors of the embodiments are in powder or polycrystalline form, growth presents no particular problem. Oxychlorides, for example, may be prepared by dissolving the oxides (rare earth and yttrium oxides) in hydrochloric acid, evaporating to form the hydrated chlorides, dehydrating, usually near 100°C . under vacuum, and treating with Cl_2 gas at an elevated temperature (about 900°C). The resulting product can be the one or more oxychlorides, with a trichloride depending on the dehydrating conditions, vacuum integrity and cooling conditions. The trichloride melts at the elevated temperature and may act as a flux to crystallize the oxychlorides. The YOCl structure is favoured by high Y contents, intermediate dehydration rates and slow cooling rates while more complex chlorides such

as $(\text{Y}, \text{Yb})_3\text{OCl}_7$, are favoured by high rare earth content, slow dehydration and fast cooling. The trichloride is subsequently removed by washing with water. Dehydration should be sufficiently slow (usually 5 minutes or more) to avoid excessive loss of chlorine.

Oxybromides and oxyiodides may be prepared by similar means using hydrobromic acid and gaseous HBr or hydroiodic acid and gaseous HI in place of hydrochloric acid and Cl_2 in the process.

Lead or alkaline earth fluorochloride or the corresponding fluorobromide may be prepared simply by melting the appropriate halides together in vacuum. The products can, in turn, be melted together with the oxyhalide.

The importance of the embodiments is the use of a host matrix for the activator and sensitizer ions having at least two different anions or at least one anion vacancy in at least one per cent of the anion sites.

The oxychlorides, oxybromides and oxyiodides are preferred embodiments of the structures involved and, of these, the oxychlorides are the preferred class. The latter consists of at least two varieties although others are not to be construed as excluded. These have various structures including (a) the tetragonal $\text{D}'_{4h}/\text{P4}/\text{mmm}$ structure in common with YOCl or (b) a hexagonal structure, with an oxygen to chlorine ratio of less than one, for which a composition with the analysed metal ratios: $\text{Y}=56\%$, $\text{Yb}=43\%$ and $\text{Er}=1\%$, lattice constants $a_0=5.607$ and $c_0=9.260$ and prominent d-spacings of 9.20, 2.33, 3.09, 4.62 and 2.83 are typical. Analyses indicate a structure $(\text{RE})_3\text{OCl}_7$, where $\text{RE}=\text{Rare Earths}+\text{Y}$, for the latter. Of these two structures, (b) is preferred due to a greater range of fluorescent characteristics and is generalised as Y_2OCl_7 for simplification herein.

While the structural considerations are paramount, the compositions preferably contain the requisite ion pair $\text{Yb}^{3+}-\text{Er}^{3+}$, $\text{Yb}^{3+}-\text{Ho}^{3+}$, mixtures thereof, or $\text{Yb}^{3+}-\text{Tm}^{3+}$. As described in conjunction with FIG. 2, initial transfer of energy is to Yb^{3+} . A minimum of this ion is set at 5% based on total cation content, since appreciably below this level transfer is insufficient to produce an expedient output efficiency regardless of the erbium content. A preferred minimum of about 10% on the same basis may, under appropriate conditions, result in an output intensity competitive with the best gallium phosphide diode. For a ytterbium content above 80%, however, brightness does not increase substantially with increasing ytterbium; and this level, therefore, represents a preferred maximum.

It has been noted that the strong fluorescence of Er may vary from essentially pure green emission at about $0.55\text{ }\mu$ to a mixture of green and red, the latter at about $0.66\text{ }\mu$. Due to the effect of exchange coupling of Yb

to Er on internal relaxation, red emission from erbium becomes dominant for larger ytterbium concentration. Generally, ytterbium concentration between about 20% and 50% results in mixed green and red output while amounts in excess of about 50% under most circumstances, result in output approaching pure red. A preferred range for a red emitting phosphor coating, therefore, lies between 50% and 80% Yb³⁺.

The erbium range is from 1/16% to 20%. Below the minimum, erbium output is not appreciable. Above the maximum, which is only approached for high Yb concentrations, internal radiationless processes substantially quench erbium output. A preferred range is from about 1/4% to about 2%. The minimum is dictated by the subjective criterion that only at this level does a coated diode with sufficient brightness for observation in a normally lighted room result. The upper limit results from the observation that further increases does not substantially increase output.

Holmium, recommended as an adjunct to erbium in conjunction with ytterbium, as well as with ytterbium alone, may be included in an amount from 1/50% to 5% to obtain green emission or to aid the green output of erbium. Such activation may be desirable in the intermediate 20% to 50% Yb range alone or when erbium is present as well as at greater concentrations of the Yb. Lesser amounts of holmium produce little discernible output as viewed by the eye. Amounts substantially larger than 2% result in no substantial increase and above about 5% result in substantial quenching. Thulium may also activate the oxychlorides, and its value is premised on its blue output. Amounts of from 1/16% to 5% are effective. Limits are derived from the same considerations discussed with holmium.

In addition to Yb+Er+Ho+Tm, "inert" cations may be included. Such cations desirably have no absorption levels below any of the levels relevant to the described multiphoton processes. A cation which has been found suitable is yttrium. Others are Pb²⁺, Gd³⁺, Na⁺ as well as other such ions listed above.

Other requirements are common to phosphor materials in general. Various impurities which may produce unwanted absorption or which may otherwise "poison" the inventive systems are to be avoided. As a general premise, maintaining the compositions at a purity level resulting from use of starting ingredients which are three nines pure (99.9%) is adequate. Further improvement, however, results from further increase in purity at least to the five nines level.

Compositions herein contain two or more different anions in at least 1% of the unit cells or equivalent anion vacancies. The aniso-

tropic crystal field conditions resulting from different anion site occupancies in the same unit cell tend to increase overall quantum efficiency. However, it is noted that as little as 1% of such cells provides significant improvement of properties. While the advantages gained by the use of the embodiment materials are largely premised on increased brightness for equivalent conditions such as doping levels, it has also been noted that visible emission may be at a variety of or combination of wavelengths. On the basis of a large number of experimental runs, some of which are represented below, it has been observed that red Er³⁺ emission is enhanced by the presence of oxygen. In fact, as noted, for the simple oxychloride with a 1:1 anion ratio, only red emission is apparent to the eye under most conditions.

It has also been observed that the presence of chlorine results in a significant improvement in overall brightness, again, for equivalent doping and pump levels. This effect is essentially independent of the prevalent colour of the visible output. Accordingly, a simple oxychloride is brighter in the red than is a simple oxybromide which is also red. A fluorochloride which emits largely in the green is brighter than is the equivalent fluorobromide.

Examples

The following specific examples were selected from a larger number to represent the more significant compositional variations. While the preparatory procedure is described in detail in the first two examples, such description in each succeeding example is considered unnecessarily repetitious. It is believed that the general preparatory technique described above is sufficient to enable a worker in the field to reproduce any composition within the range of the embodiments.

Example 1

A composition represented nominally as



was prepared from the following starting ingredients.

Y ₂ O ₃	1.58	grams	
Yb ₂ O ₃	1.14	grams	
Er ₂ O ₃	0.038	grams	115

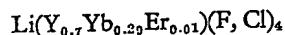
All materials were particulate to facilitate dissolution. The oxidic materials were next dissolved in hydrochloric acid and this solvent was next evaporated to leave the mixed rare earth hydrated chloride. The residue was dried in air to remove unbonded (excess) H₂O. The resulting material was next placed in a quartz tube which was connected to a vacuum station after which tube and con-

tents were maintained at 100°C under vacuum for a period of four hours to remove water of hydration. With tube and contents still connected to the vacuum station, temperature was raised to 1000°C. to produce a molten mixture of rare earth trichloride and rare earth oxychloride. The contents were next cooled and the trichloride was removed by dissolving in water. Crystals of the approximate composition set forth were produced by spontaneous nucleation during cooling.

Crystals of the final composition were admixed with collodion and the composite was painted on the surface of a silicon doped gallium arsenide diode capable of emitting at an infrared wavelength at about 0.93 μ when forward biased. The diode was biased at about 1 volt in the forward direction under which conditions current flow was observed to be about 1 ampere. The coated portion of the diode glowed an apparent yellow-red colour (spectroscopically observed to represent a measure of green and red wavelengths). Quantum efficiency (visible output divided by infrared absorbed by the phosphor) was estimated to be at a level in excess of 20%. Note: Maximum quantum efficiency for the prevalent third-photon transition is 33 1/3% since three quanta of infrared are by definition required to produce one quantum of visible output.

Example 2

The approximate composition,



was produced from the following starting ingredients:

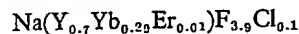
	Y_2O_3	1.58 grams
	Yb_2O_3	1.14 grams
	Er_2O_3	0.038 grams
40	LiCl	0.85 grams

The particulate starting materials were dissolved in hydrochloric acid. Hydrochloric acid was added resulting in the precipitation of white powder. The solvent was next removed by evaporating at 50°C. The powder was again placed in a quartz tube and contents were dried under vacuum at 100°C for four hours to remove water of hydration. The temperature was again raised to 1000°C to melt the product. Tube and contents were permitted to cool so as to result in a particulate end product of the scheelite structure.

The powder was again mixed with collodion to minimize scatter loss and the mixture was painted on to a gallium arsenide diode as in Example 1. Under one-volt forward bias (as in Example 1), emission was green and of an efficiency comparable to Example 1.

Example 3

The composition represented by the approximate formula



was prepared by melting together at about 1300°C. an intimate mixture of

NaCl	0.058 grams
NaF	0.378 grams
YF_3	1.022 grams
YbF_3	0.666 grams
ErF_3	0.022 grams

The final product had a structure similar to the Na_2ThF_6 structure. This product too was mixed with collodion and was painted on a GaAs diode which was biased as in Example 1. Colour and apparent brightness were as in Example 2.

Additional Examples

The following compositions were prepared in the general manner described above and were all exposed to infrared emission from a forward biased 0.93 μ GaAs diode. Compositions are set forth in tabular form in terms of their approximate formulas, and apparent colours are indicated based on bias levels equivalent to those utilized in the above examples. The apparent colours were as set forth. While not indicated, many of the phosphors could be made to yield a range of apparent colours by changing the bias conditions on the diodes.

TABLE

$\text{Yb}_{0.99}\text{Er}_{0.01}\text{OCl}$	Red	
$(\text{Yb}_{0.99}\text{Er}_{0.01})_3\text{OCl}_7$	Red	
$\text{Yb}_{0.995}\text{Ho}_{0.005}\text{OCl}$	Green	
$(\text{Yb}_{0.995}\text{Ho}_{0.005})_3\text{OCl}_7$	Green	95
$\text{Yb}_{0.995}\text{Tm}_{0.005}\text{OCl}$	Blue	
$(\text{Yb}_{0.995}\text{Tm}_{0.005})_3\text{OCl}_7$	Blue	
$(\text{Yb}_{0.5}\text{Y}_{0.49}\text{Er}_{0.01})\text{OCl}$	Red	
$\text{Yb}_{0.5}\text{Y}_{0.49}\text{Ho}_{0.01}\text{OCl}$	Green	
$\text{Yb}_{0.5}\text{Y}_{0.49}\text{Tm}_{0.01}\text{OCl}$	Blue	100
$(\text{Yb}_{0.5}\text{Y}_{0.49}\text{Er}_{0.01})_3\text{OCl}_7$	Red	
$(\text{Yb}_{0.5}\text{Y}_{0.49}\text{Ho}_{0.01})_3\text{OCl}_7$	Green	
$(\text{Yb}_{0.5}\text{Y}_{0.49}\text{Tm}_{0.01})_3\text{OCl}_7$	Blue	
$\text{Yb}_{0.16}\text{Y}_{0.84}\text{Er}_{0.01}\text{OCl}$	Red	
$(\text{Yb}_{0.16}\text{Y}_{0.84}\text{Er}_{0.01})_3\text{OCl}_7$	Red	105
$(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})_3\text{OCl}_7$	Red	

TABLE (Cont.)

	$\text{Li}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}$	Green	$\text{Li}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2$	Green	
	$\text{Na}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}$	Green	$\text{Na}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2$	Green	
	$\text{K}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}$	Green	$\text{K}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2$	Green	
5	$\text{Rb}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}$	Green	$\text{Rb}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2$	Green	10
	$\text{Cs}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}$	Green	$\text{Cs}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2$	Green	
	$\text{Li}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{Na}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{K}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
15	$\text{Rb}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{Cs}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{3.9}\text{Cl}_{0.1}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{Li}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{Na}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{K}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
20	$\text{Rb}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{Cs}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_2\text{Cl}_2(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{OCl}$	Red			
	$\text{Na}(\text{Yb}_{0.29}\text{Y}_{0.7}\text{Er}_{0.01})\text{F}_{2.9}\text{Cl}_{0.1}$	Green			

Where the phosphor is included as an adherent coating on a diode, it may be desirable to include some inert material (inert from the phosphorescent standpoint). Such material may serve to improve adhesion between the phosphor and the diode and/or may serve the function of reducing light scattering between particles in a coating or between the diode and the particles.

For the latter use, it is, of course, desired that the "inert" material have a refractive index which is approaching or exceeding that of the phosphor. In some cases, an inert material with an index approximating that of the GaAs is preferred. Typical index values for this purpose are approximately 2 to 3.5 on the usual scale in which vacuum is graded as unity.

Where such additional material is incorporated in a phosphor coating, the amount is desirably kept to a minimum sufficient for the intended purpose, be it to enhance adhesion and/or to reduce scattering. Since this additional material is inert from the phosphorescent standpoint, it otherwise acts only as a diluent and so reduces the overall quantum efficiency of the overall device.

WHAT WE CLAIM IS:—

1. An electroluminescent device for producing radiation in the visible spectrum including a semiconductor p-n junction diode capable of producing infrared radiation when biased, said diode being provided with a phosphor on a surface thereof for converting said infrared radiation to radiation in the visible spectrum, the said phosphor consisting of an oxyhalide and/or a fluorohalide host material, the halide in the fluorohalide being other than fluoride, and containing at least 5 cation percent of Yb^{3+} based on the total cation content of the phosphor, in which either the phosphor contains at least two anion sites per unit cell which are differently populated in at least one percent of the unit cells of said phosphor, or there is at least one anion vacancy per unit cell in at least one percent of the unit cells of the said phosphor, and wherein the phosphor further contains at least one of the following cations in the specified concentration ranges, selected from the group which consists of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} , from 1/50 cation % Ho^{3+} to 5 cation % Ho^{3+} and 1/16 cation % Tm^{3+} to 5 cation % Tm^{3+} .

2. A device as claimed in claim 1, wherein the phosphor includes at least a 1/4 cation % Er^{3+} .
- 5 3. A device as claimed in claim 1 or claim 2, wherein the phosphor includes not more than 2 cation % Er^{3+} .
4. A device as claimed in any one of claims 1—3, wherein the phosphor includes not more than 2 cation % Ho^{3+} .
- 10 5. A device as claimed in claim 1, wherein the phosphor contains at least 10 cation % of Yb^{3+} based on the total cation content of the phosphor.
6. A device as claimed in any one of the preceding claims wherein the said compound is an oxychloride.
7. A device according to claim 6, wherein the said oxychloride compound has an oxygen to chlorine ratio of less than one.
- 15

K. G. JOHNSTON,
Chartered Patent Agent,
5 Mornington Road,
Woodford Green, Essex.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

